

Mechanisms of biogenic nanocrystalline uraninite oxidation in the presence of Fe(III)(hydr)oxides

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Uranium's fate and mobility in the environment will be determined in part by its oxidation state with the more reduced form of uranium (U(VI)) often existing as a solid-phase compared to the highly mobile U(VI), commonly present in the aqueous phase. Subsurface bacteria including sulfate reducing bacteria (SRB) and iron reducing bacteria (IRB) can reduce soluble U(VI) to insoluble U(IV) with subsequent precipitation of UO_2 . However, it has been shown that SRB-mediated uraninite nanocrystals can be reoxidized (and thus remobilized) by Fe(III)-(hydr)oxides, common constituents of soils and sediments, once available electron donor is exhausted. This UO_2 reoxidation has also been shown to occur under sulfate reducing conditions; however the mechanism of this process remains unresolved. Under elevated sulfide levels, following sulfate reduction, UO_2 and sulfide compete for oxidation by available Fe(III), thus the extent of U(IV) reoxidation is linked to both Fe and sulfide concentrations in this system.

Experiments were performed with *Desulfovibrio desulfuricans* G20 to investigate biotic influences on the system. Following growth of G20 in lactate-limited medium containing 0 or 180 μM U(VI) and sulfate, previously produced and cleaned biogenic UO_2 was added to systems without U(VI) to compare rates of U(IV) reoxidation in the presence of hematite. Following 10 d of incubation, soluble U(VI) was detected only in systems that began with U(VI). These results suggest differences in reactivity between previously precipitated and cleaned UO_2 and freshly reduced UO_2 .

Why are chalk particles so small?

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In nature, many systems do not reach equilibrium. Sea water, for example, is oversaturated with respect to calcite. And chalk, composed of countless tiny calcite coccolith fragments, challenges diagenesis. Individual crystals remain $<1 \mu\text{m}$ in diameter. In my lab, I can make calcite crystals from CaCl_2 and Na_2CO_3 solutions that are 5 times this size after only one day. Why has Ostwald ripening failed the tiny chalk particles for more than 60 million years? Thermodynamics works. There must be reasons we cannot see, that keep these biogeochemical systems far from equilibrium.

In this special session commemorating the 5th birthday of *Elements*, it is fitting to look back on some of the themes and see how they extend into today's research. Chalk is a reservoir for drinking water and hydrocarbons, so its behaviour has a bearing on *Sustainability* and *Energy*. The issues of *CO₂ in the atmosphere and oceans*, and *Mineral surfaces and the origin of life*, link to biomineralisation, also a hot topic. And the tools of *Nanogeoscience* allow us to see at scales that were only dreamed of, just a few decades ago.

If our data suggest thermodynamics has failed, closer examination at the solid-fluid interface should offer insight.

On chalk particles in aqueous solution, atomic force spectroscopy reveals hydrophobic compounds that vary in composition over scales of 10's of nanometers, so the calcite is not really in contact with the solution. Time resolved dissolution of individual coccoliths reveals the differences in behaviour of biogenic and inorganic calcite. After calcite has dissolved, an organic remnant remains, demonstrating that coccoliths are covered by a protective coating. Algae control biomineralisation with complex polysaccharides. Compounds extracted from cultured algae still inhibit calcite growth. So the free energy drive of small chalk fragments to become large, the recrystallisation that defines diagenesis, is hindered by sugar.

With molecular modelling, we explored polysaccharide bonding properties. Once OH functional groups contact calcite, they do not leave again. We investigated the nature of OH bonding using ethanol, the simplest organic molecule that has both hydrophobic and ionic ends. Several surface sensitive techniques demonstrated that $\text{CH}_3\text{CH}_2\text{OH}$ forms an impermeable, hydrophobic layer that inhibits water penetration and that ethanol structures the solution, well out into the bulk liquid, preventing equilibrium calcite growth.

Thermodynamics works, also for biogeochemical systems, provided we include all the components!